DISTRIBUTION OF AMINO ACIDS IN LUNAR REGOLITH. J. E. Elsila[1], M.P. Callahan[1], D.P. Glavin[1], J.P. Dworkin[1], S.K. Noble[1], and E.K. Gibson, Jr.[2], [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771, [2]ARES, NASA/Johnson Space Center, Mail Code KA, Houston, TX 77058. Email: Jamie.Elsila@nasa.gov

Introduction: One of the most eagerly studied questions upon initial return of lunar samples was whether significant amounts of organic compounds, including amino acids, were present. Analyses during the 1970s produced only tentative and inconclusive identifications of indigenous amino acids (e.g. [1],[2]). Those analyses were hampered by analytical difficulties including relative insensitivity to certain compounds, the inability to separate chiral enantiomers, and the lack of compound-specific isotopic measurements, which made it impossible to determine whether the detected amino acids were indigenous to the lunar samples or the results of contamination. Numerous advances have been made in instrumentation and methodology for amino acid characterization in extraterrestrial samples in the intervening years, yet the origin of amino acids in lunar regolith samples has been revisited only once for a single lunar sample [3] and remains unclear.

Here, we present initial data from the analyses of amino acid abundances in 12 lunar regolith samples. We discuss these abundances in the context of four potential amino acid sources: (1) terrestrial biological contamination; (2) contamination from lunar module (LM) exhaust; (3) derivation from solar wind-implanted precursors; and (4) exogenous delivery from meteorites.

Analytical techniques and samples: We analyzed 12 lunar regolith samples (Table 1). Five samples were allocated from the pristine lunar collection at NASA Johnson Space Center (JSC), while the remaining seven had previously been allocated to Dr. Everett Gibson and had resided in his laboratory for many years. The samples spanned a range of maturities as measured by I_s/FeO ratio [4] and included two samples from Apollo 17 that were collected to test exposure to the lunar module exhaust. Three regoliths had been previously analyzed for amino acid content.

Regolith samples were analyzed using previously published methods [5]. Portions (masses ranged from ~250 to 800 mg) of the lunar regolith powders were extracted in ultrapure water. Half of each extract was hydrolyzed with HCl acid vapor to release or create amino acids from precursors. Both the unhydrolyzed and hydrolyzed extracts were then desalted with cation-exchange resin. Amino acid abundances and distributions were analyzed via ultrahigh-performance liquid chromatography with fluorescence detection and time-of-flight mass spectrometry following derivatization with *o*-phthaldialdehyde/N-acetyl-L-cysteine.

Table 1. Lunar regoliths investigated in this study

Sample	Is/FeO ratio (maturity) [4]	Amino acid analysis
61221	9.2, immature	This study
73131[a]	16, immature	This study
73241[a]	18, immature	This study
78501	36, submature	This study
73141	48, submature	This study
70011[a,b]	54, submature	This study, [6],[7]
76501	58, submature	This study
15271	63, mature	This study
15261	77, mature	This study
72501[a,c]	81, mature	This study, [6],[7]
78421[a]	92, mature	This study, [3]
69961	92, mature	This study

[a]New (pristine) allocation
[b]Collected beneath LM as an exhaust-exposed sample
[c]Collected 6.5 km from LM as LM exhaust control

Results and Discussion:

Amino acid abundances and curation effects: Amino acids were detected in all 12 regolith samples, with total concentrations ranging from 0.3 to 139 parts-per-billion (ppb) in the unhydrolyzed extracts and 105 to 1910 ppb for the hydrolyzed extracts. There were distinct differences between the new allocations from the JSC curation facility and those samples that had been stored outside of the curation facility in a separate laboratory. The laboratory-stored samples contained higher concentrations of the amino acids γ-amino-*n*-butyric acid (γ-ABA) and ε-amino-*n*-caproic acid (ε-ACA) compared to the curated samples. The hydrolyzed extracts from the laboratory samples also contained roughly racemic mixtures of D-serine and L-serine (D/L ~ 1), while those of the JSC-curated samples contained more L-serine (D/L = 0.04 to 0.25). These differences may reflect contamination of the laboratory-stored samples during the past >35 years. The source of the contamination remains unknown, although ε-ACA is a monomer released upon hydrolysis of Nylon-6, commonly found in the storage bags used for curation [8]. In the remainder of this abstract, we focus on the data from the five JSC-curated samples (70011, 72501, 73131, 73241, and 78421).

Amino acid distributions: Amino acids detected in the hydrolyzed extracts of all five curated samples were glycine, β-alanine, D- and L-alanine, α-aminoisobutyric acid (AIB), and ε-ACA. In addition, several other amino acids were detected in one or more samples, including D-and L-β-amino-*n*-butyric acid, α-amino-*n*-

butyric acid (enantiomers not separated), γ-ABA, D- and L-aspartic acid, glutamic acid (enantiomers not separated), D- and L-serine, L-threonine, and L-valine. The detection of AIB is notable because it is a common meteoritic amino acid that is rare in the terrestrial biosphere; it is often used to argue for the indigenous nature of amino acids in carbonaceous chondrites. A tentative identification of AIB was previously made in sample 78421 [3] with a concentration of ≤0.3 ppb, but this is the first confirmed detection in a lunar sample. We detected AIB with concentrations of 0.7 to 1.6 ppb in the hydrolyzed extracts. Another amino acid that is rare in the terrestrial biosphere but common in carbonaceous chondrites is isovaline [9]; we did not detect isovaline in any of the lunar samples.

Hydrolyzed vs. unhydrolyzed samples: In these five regolith samples, we observe a marked increase in amino acid abundance upon hydrolysis, with the percentage of free amino acids (detected in the unhydrolyzed extract) ranging from 0.05% to 43% (Table 2). In carbonaceous chondrites, this value is typically in the 30% to 60% range [e.g., 10]. The large increase upon acid hydrolysis in certain samples suggests creation or liberation of amino acids from a precursor. This precursor could be a protein from terrestrial biological contamination, and the predominance of L- over D-enantiomers in several proteinogenic amino acids suggests that this is a likely possibility. However, such a range in the percentage of free amino acids among samples that have been curated under the same conditions and protocols in the same facility suggests that other precursors may also be present. Alternatively, the amino acids could be formed by hydrolysis of hydrogen cyanide (HCN) polymer. HCN could be implanted in the regolith by the solar wind (see below for further discussion) and polymerized during hot-water extraction [11]. HCN was also one of the primary volatiles in the LM exhaust [12]; the LM-exposed (70011) and the LM-control (72501) samples, however, had similar free and hydrolyzed amino acid abundances, with the smallest increases in abundances upon hydrolysis of the samples in our study (see Table 2). This argues against HCN from the LM exhaust as a precursor to the amino acids released upon hydrolysis.

Correlation with sample maturity: We compared amino acid abundance to sample maturity, as measured by I_s/FeO ratio [4]. Soil maturity correlates with surface exposure and, hence, exposure to solar wind; therefore, correlation between amino acid abundance and maturity would suggest a solar-wind-implanted origin of amino acid precursors. Intriguingly, opposite trends emerged for the hydrolyzed and unhydrolyzed samples. In the unhydrolyzed extracts, the least mature samples analyzed contained the lowest levels of amino acids (Table 2). In the hydrolyzed extracts, the least mature samples had the highest amino acid concentrations. This observation suggests that the least mature samples contained some acid-hydrolyzable amino acid precursor in greater abundances than the more mature samples, which is in conflict with the solar wind as the source of this precursor. One possible explanation is that increased surface exposure should also correlate with exposure to cosmic radiation, which could degrade volatiles. Biological contamination also remains a possible amino acid source, with the observed correlation with soil maturity being coincidental.

Table 2. Comparison of free and total amino acid abundances in lunar regoliths of various maturities.

Sample	I_s/FeO	Free (ppb)	Total (ppb)	% Free
73131	16	5.1	494.0	1.0%
73241	18	0.3	651.2	0.05%
70011	54	33.8	106.4	32%
72501	81	42.7	105.3	43%
78421	92	12.0	157.6	7.6%

Future directions: We have confirmed and expanded on earlier detections of amino acids in lunar regoliths. However, the origin of these amino acids remains undetermined. Compound-specific isotopic measurements should help distinguish between potential sources of these compounds, as the isotopic signatures of biological contamination, solar wind precursors, and meteoritic infall should be distinct. The need for such measurements was acknowledged in previous analyses [3]; instrumental capabilities did not then exist, but have since been developed. Planned future isotopic measurements, combined with the data on amino acid abundances and distributions in this initial study, should help to answer the decades-old questions about the presence and origin of lunar amino acids.

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